

PATENT SPECIFICATION

DRAWINGS ATTACHED

(11) 1255551



- (21) Application No. 15639/69 (22) Filed 25 March 1969
 (31) Convention Application No. P 17 71 077.9
 (32) Filed 30 March 1968 in
 (33) Germany (DT)
 (45) Complete Specification published 1 Dec. 1971
 (51) International Classification C 03 c 17/02 // H 01 17/44
 (52) Index at acceptance
 C1M 5A 5D10 5D12 5D16 5D7 5D8 D22 S10B S19
 H1K 211 217 358 54Y 581 638

(54) IMPROVEMENTS IN OR RELATING TO EXTERNALLY
 COATED FUSED SILICA TUBES

(71) We, HERAEUS-SCHOTT QUARZSCHMELZE GMBH., a German Body Corporate, of 8 Rohrstrasse, Hanau, Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fused silica tubes, more particularly for carrying out semiconductor technological methods, which have an external coating.

It is known in the manufacture of semiconductors such as diodes, four layer diodes, transistors, integrated circuits or the like, to utilise diffusion techniques for doping purposes, for example. In such manufacture, a diffusion tube made of fused silica is used, which is arranged in an electrically heated furnace. In the diffusion tube which contains the semiconductor crystals to be doped, the predetermined gas environment for doping the semiconductor crystals is maintained at a predetermined diffusion temperature.

We are aware that French Patent specification 1 293 554 describes a diffusion tube made of fused silica which has an external coating. This coating becomes molten at the temperatures at which the semiconductor crystals are treated and the purpose of this is to avoid impurities diffusing through the fused silica diffusion tube into the semiconductor treatment space, i.e. the space surrounded by the fused silica tube.

It has been ascertained that diffusion tubes made of fused silica which have been used up to now and remaining permanently in the furnace have a disadvantage which consists in that the diffusion tube distorts plastically if the diffusion temperature is too high. The result of this distortion is that support gates loaded with the semiconductor crystals can no longer pass into the diffusion tube, so that a frequent replacement of the diffusion tube is unavoidable.

We are also aware that United States Patent [Price 25p]

specification 3 275 493 describes an arrangement for raising the mechanical strength of glass bodies by providing such body with a mixed coating such as Cordierite subjected to compressive stress. This proposal cannot be applied to fused silica diffusion tubes, however, because at temperatures higher than 1000°C, the coating becomes soft and the compressive stresses existing in the coating would have balanced themselves out.

The invention has for its object to produce a fused silica tube, more particularly for carrying out various treatments on semiconductors which can be effected at temperatures of more than 1000°C, without any danger of undesirable distortions.

The invention consists in a fused silica tube capable of being subjected to temperatures in excess of 1000°C, wherein at least that part of the tube which is to be subjected to such temperatures has a coating consisting of a continuous fine layer of crystalline silica e.g. Cristobalite whose thickness is less than 5% of the wall thickness of the fused silica tube in the region of the coating. Preferably the layer thickness is less than 1%, of the said wall thickness.

It was surprising that the fused silica tubes according to the invention with the Cristobalite coating, did not break when a temperature variation in the region of 300°C whether upwardly or downwardly was exceeded although, as known per se, for example Cristobalite has in this temperature range due to an alteration in modification, a sudden transition as regards its coefficient of expansion. Presumably, this relates to the fact that the coating made of fine crystalline Cristobalite is extremely thin.

The fused silica diffusion tube of the invention with the Cristobalite coating exhibited no severe plastic distortion during a period of several weeks, at temperatures which reached approximately 1300°C. The particularly good mechanical strength of the fused silica diffusion tube of the invention, also at temperatures

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exceeding 1000°C, is probably explained by the fact that the applied fine crystalline coating is continuous and the crystals still grow at high temperatures.

5 It has also been proved advantageous to provide a protective coating on the Cristobalite. This avoids impurities penetrating the fused silica tube, for example, from the muffle of the furnace during the heating up of the fused
10 silica diffusion tube to the temperature at which the semiconductor doping is carried out, which would trigger off undesired crystallisation processes therein. Such materials have proved suitable as coating materials for the
15 protective coating which at temperatures of approximately 1300°C still do not evaporate overmuch, however, already show a plastic behaviour. For example, germanium oxide, mixtures of germanium oxide and silicon oxide
20 or mixed glasses have proved to be very suitable.

In order that the invention may be more clearly understood, reference will now be made to the accompanying drawings which show
25 some embodiments thereof by way of example, and in which:—

Figure 1 shows in elevation a fused silica tube constructed in accordance with the invention,

30 Figure 2 shows a cross-section through the fused silica tube of Figure 1 in the region of the coating, and

Figure 3 shows a cross-section through a fused silica tube with such coating and also
35 a protective layer.

Referring now to the drawings, a fused silica tube 1 is, as shown in Figure 1, partly provided with a coating 2 made of a continuous, fine layer of crystalline silica e.g. Cristobalite.
40 It is, of course, also possible to coat the whole of the fused silica tube with the fine crystalline layer. Advantageously, the fine crystalline layer is only applied to those parts which are subjected to high temperatures of more than
45 1000°C. By partly coating the fused silica tube there remains, for example, the possibility to retain on the uncoated parts, more particularly the ends of the tube, fused silica sections or to insert other parts made from fused silica.

50 The fused silica tube 1 shown in Figure 3 in cross-section has not only a coating 2 of Cristobalite but also has a protective layer 3 applied to such coating e.g. of germanium oxide, a mixture of germanium oxide and silicon

oxide or of a mixed glass, which becomes plastic at a temperature of approximately 1300°C.

The manufacture of fused silica tubes provided with a fine crystalline coating can be effected by spraying a very pure fine crystalline material such as Cristobalite in powder
60 form onto the fused silica tube and then heating it by a flame or in a furnace. The quartz glass tube is maintained at a high temperature for a period until a coherent layer of Cristobalite is formed. In a fused silica tube whose
65 wall thickness in the region of the crystalline coating, amounts to approximately 2 mm, the thickness of the layer, for example, will amount to less than 0.02 mm.

WHAT WE CLAIM IS:—

1. A fused silica tube capable of being subjected to temperatures in excess of 1000°C, wherein at least that part of the tube which is to be subjected to such temperatures has a coating consisting of a continuous fine layer
70 of crystalline silica e.g. Cristobalite, whose thickness is less than 5% of the wall thickness of the fused silica tube in the region of the coating.

2. A fused silica tube as claimed in claim 1, wherein the layer thickness is less than 1% of the said wall thickness.

3. A fused silica tube as claimed in claim 1 or 2, wherein the fine crystalline layer is formed by applying crystalline silica in powder
85 form to the surface of the tube and then heating the tube in a flame or furnace.

4. A fused silica tube as claimed in any preceding claim, wherein a protective layer is provided on the fine crystalline layer.

5. A fused silica tube as claimed in claim 4, wherein the protective layer consists of germanium oxide, a mixture of germanium oxide and silicon oxide or of a mixed glass, which becomes plastic at a temperature of approximately
95 1300°C.

6. A fused silica tube, substantially as hereinbefore described with reference to Figure 1 and Figure 2 of the accompanying drawings.

7. A fused silica tube substantially as hereinbefore described with reference to Figure 3
100 of the accompanying drawings.

BARON & WARREN,
16, Kensington Square,
London, W.8.
Chartered Patent Agents.

